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# Tributyltin: Position Document 1

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This Position Document addresses the risks and benefits of pesticide products containing the subject active ingredient. The Agency has determined that the use of products containing the subject active ingredient may meet or exceed a risk criterion described in 40 CFR Part 154. Potential hazards will be examined further to determine the nature and extent of the risk, and considering the benefits of the subject active ingredient, whether such risks cause unreasonable adverse effects on the environment.

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# TRIBUTYLTIN: POSITION DOCUMENT 1

Office of Pesticide Programs
Office of Pesticides and Toxic Substances
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460
December 1985

## Executive Summary

This Tributyltin Support Document presents the basis for the initiation of a Special Review of all pesticide products containing tributyltin (TBT) active ingredients used as paint additives (antifoulants) to inhibit the growth of certain aquatic organisms. The TBT paints are primarily applied to boat and ship hulls. These TBT compounds include: bis-(tributyltin) oxide, bis(tributyltin) adipate, bis(tributyltin) dodecenyl succinate, bis(tributyltin) sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, and tributyltin resinate.

The initiation of the Special Review is based on the Agency's determination that the use of the TBT compounds in antifoulant paints may result in TBT exposure to nontarget aquatic organisms at concentrations resulting in acute and chronic effects. The Agency has determined that the risk criteria, as described in 40 CFR 162.11 are met or exceeded by use of these TBT antifoulant paints.

The Agency evaluated bioassay studies which indicated that the TBT compounds are highly toxic, frequently at the parts per trillion (ppt) level, to nontarget marine and freshwater aquatic organisms. Toxicity tests have found adverse affects to molluscs at levels of 60 and 100 ppt. The laboratory toxicity measure which the Agency used to evaluate the acute hazard was the median lethal concentration ($LC_{50}$) which kills 50 percent of the test organisms after a designated time period. The Agency also reviewed numerous aquatic toxicity studies which indicate that the TBT compounds cause chronic hazards such as anatomical abnormalities, growth effects, and is bioaccumulated.

Environmental monitoring data measuring TBT concentrations in the Great Lakes and U.S. coastal waters were compared to the concentrations identified as causing adverse effects in the laboratory toxicity studies. From this comparison, the Agency has determined that the risk criteria, as described in 40 CFR 162.11 are met or exceeded by use of these TBT antifoulant paints.

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# I. INTRODUCTION

## A. General Background and Organization

The Environmental Protection Agency (EPA) is initiating a Special Review of all pesticide products containing tributyltin (TBT) active ingredients used as paint additives (antifoulants) to inhibit the growth of certain aquatic organisms. The TBT paints are primarily applied to boat and ship hulls. These TBT compounds include: bis(tributyltin) oxide, bis(tributyltin) adipate, bis(tributyltin) dodecenyl succinate, bis(tributyltin) sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, and tributyltin resinate. This Tributyltin Support Document presents the basis for initiation of the Special Review on these nine active ingredients.

The EPA has determined that the pesticidal use of these compounds results in TBT exposure to nontarget aquatic organisms at concentrations resulting in acute and chronic toxicity and, when applied as antifoulant paints, meet or exceed the risk criteria as described in 40 CFR 162.11. Accordingly, a Special Review of products containing these TBT compounds and applied as antifoulant paint is appropriate to determine whether additional regulatory actions are required. During the Special Review process, EPA will carefully examine the risks and benefits of using TBT products as antifoulants. If the information reviewed indicates that use of these compounds on other sites results in exposure to nontarget aquatic organisms, the Special Review may be extended to include other pesticidal applications of these products and other TBT active ingredients with registered uses which result in aquatic acute and/or chronic effects or other effects of concern.

This Support Document contains four parts. Chapter I is this Introduction. Chapter II describes the risk to nontarget aquatic organisms resulting from the use of TBT compounds in antifoulant paints. Chapter III describes the usage and benefits of these TBT compounds. Chapter IV outlines other regulatory considerations associated with the TBT compounds.

## B. Legal Background

### 1. The Statute

A pesticide product may be sold or distributed in the United States only if it is registered or exempt from registration under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) as amended (7 U.S.C. 136 et seq.). Before a product can be registered, it must be shown that it can be used without "unreasonable adverse effects on the environment" (FIFRA section 3(c)(5)), that is, without causing "any unreasonable risk to

man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of the pesticide" (FIFRA section 2(bb)). The burden of proving that a pesticide meets this standard for registration is at all times, on the proponent of initial or continued registration. If at any time the Agency determines that a pesticide no longer meets this standard for registration, then the Administrator may cancel the registration under section 6 of FIFRA.

2. The Special Review Process

The term "Special Review" is the name being used for the process previously called the Rebuttable Presumption Against Registration (RPAR) process 40 CFR 162.11. Modifications to the process are described in the final Special Review regulations (50 FR 49003). These regulations will become effective after 60 days of continuous congressional session after the issuance of the regulations, which took place on November 19, 1985. These modifications include new risk criteria. Until these regulations are adopted, the present RPAR procedures will remain in effect as set forth in 40 CFR 162.11.

The Special Review (RPAR) process provides a mechanism through which the Agency gathers risk and benefit information about pesticides which appear to pose risks of adverse effects to human health or the environment which may be unreasonable. Through issuance of notices and support documents, the Agency publicly sets forth its position and invites pesticide registrants, USDI, USDA, FDA, user groups, environmental groups, and other interested persons to participate in the Agency's review of suspect pesticides.

Risk evidence, submitted to and/or gathered by the Agency, must be evaluated and considered in light of the benefit information. If the Agency determines that the risks appear to outweigh the benefits, the Agency can initiate action under FIFRA to cancel, suspend, and/or require modification of the terms and conditions of registration.

C. Chemical Background

1. Registered Uses and Production

There are 20 tributyltin compounds registered as pesticidal active ingredients. Nine of the TBT compounds are registered for use in antifoulant paints. Other registered uses of the TBT's include but are not limited to: use as wood preservatives, textile biocides, disinfectants, use in cooling towers, paper and pulp mills, and leather processing facilities. Current annual domestic production of TBT pesticides for these uses is estimated at approximately 730,000 to 860,000 pounds of active



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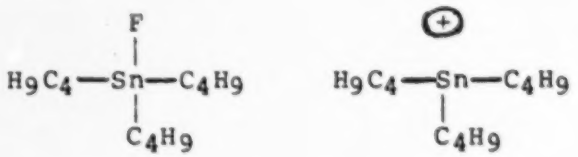
ingredient for the 20 TBT active ingredients. Approximately a third of the TBT is used in antifoulant paints, one third is used in wood preservatives, and the remaining third is used in other pesticidal formulations.

2. Chemical and Physical Characteristics of TBT's in Antifouling Paints

The tributyltin antifouling paints are chemically characterized by a tin (Sn) atom covalently bonded to three butyl ($C_4H_9$-) moieties. A representative TBT active ingredient, tri-n-butyltin fluoride, may be chemically described by the following structural formulas for the undissociated (neutral) pure form of the active ingredient and for the water dissociated (positively charged) form:



Elemental or inorganic forms of tin (as in mineral deposits or tin cans) appear to cause negligible toxicological effects in man or wildlife. However, in contrast, the TBTs display an increased fat solubility and consequently, enhanced ability to penetrate biological membranes, thereby posing a greater toxicity and environmental risk (Thayer 1984). When tributyltin is used as an active ingredient in antifouling paint formulations that are applied for example to boat hulls, the free TBT ion is leached or released from the paint, providing fresh toxicant at the wetted paint surface to inhibit growth of fouling organisms (e.g., barnacles, tubeworms).

Table 1 identifies the nine tributyltin active ingredients under consideration in the Special Review and their Chemical Abstract Service (CAS) number.

In general, the TBT antifouling paints may be classified into two categories according to the way the tributyltin moiety is incorporated into the paint coating and subsequently released. In the first group, the conventional freely associated coatings (e.g., TBT oxide or fluoride), the biocide is physically incorporated into the paint matrix (which contains the pigment, water-soluble resins, and inert substances). Upon contact with the marine environment, the surface particles of the paint coating are dissolved with physical release of the toxic TBT by diffusion. This category of TBT antifoulant coatings have traditionally posed a problem of a high early release rate with subsequently shortened time period of protection from attachment and growth of fouling organisms (Fisher et al. 1981). In the second category, the copoylmer paints, the TBT moiety is chemically

Table 1. Tributyltin Active Ingredients as Used in Antifoulant Paints

| Chemical Name | Chemical Abstract Service Number |
|---|---|
| bis(tributyltin) oxide | 56-35-9 |
| bis(tributyltin) dodecenyl succinate | 12379-54-3 |
| bis(tributyltin) sulfide | 4804-30-4 |
| tributyltin acetate | 56-36-0 |
| tributyltin acrylate | 13331-52-7 |
| tributyltin fluoride | 1983-10-4 |
| tributyltin resinate | none assigned |
| tributyltin methacrylate, and copolymer | 2155-70-6, and 26345-187 |
| bis(tributyltin) adipate | 7437-35-6 |

bonded to a polymer backbone (e.g., TBT methacrylate copolymer). This bond is designed to be hydrolytically unstable under slightly alkaline conditions. Therefore, the biocide is released only by chemical hydrolysis of the tributyltin itself. This attachment (pendant polymer) accounts for several advantages: 1) release is governed by hydrolysis of the TBT group rather than dissolution of the paint particle, 2) the release rate can be better controlled (slowed down) by alteration of the polymer's water absorption characteristics, and 3) the formulation is safer for shipyard personnel to handle because the biocide is released only when wetted and also the polymeric form poses less irritation to skin and nasal passages. With the exception of the initial high release rate during the "conditioning" period (approximately the first month after the freshly painted hull is placed in the water), these polymeric, film-forming resin coatings are characterized by a slow dissolution rate from ship hulls and thus the ability to achieve a constant but prolonged, low release rate of antifouling toxicant (ibid.).

In general, toxicity of organotin compounds to aquatic organisms is thought to increase with the number of butyl substituents from one to three (Laughlin, Norlund, and Linden 1984) and then to decrease with the addition of a fourth butyl group. In order to assess the fate of a particular tributyltin derivative in water one must consider the dissociated active form, the TBT cation ($Bu_3Sn^+$), and its major metabolites presumably formed by progressive debutylation to inorganic tin (Blunden 1984).

$$Bu_3Sn^+ \rightarrow Bu_2Sn^{2+} \rightarrow BuSn^{3+} \rightarrow Sn^{4+}$$

In addition, Matthias and coworkers (1985) have prepared a manuscript for publication (currently in review by Analytical Chemistry) containing their findings of relatively high levels of tetrabutyltin in surface (microlayer) water samples from Baltimore harbor. This species ($Bu_4Sn$) could possibly be formed from microbial/photolytic transformation of the tri- and dibutyl forms which could then be reconverted to the dibutyl species. The tetrabutyltin species may also be present in some paint formulations as an impurity in the manufacturing process. Also, butylmethyltin ($Bu_3MeSn$) has been isolated from marine sediment samples (ibid.).

Analytical methodology suitable for environmental monitoring must, in view of the foregoing discussion, be able to detect at low levels all butyltin and mixed methylbutyltin species arising from degradation of the TBT cation in marine and fresh-water environments. Furthermore, because morphological and toxicological effects have been found to occur in nontarget aquatic organisms when exposed to TBT concentrations in the parts per trillion (ppt) range, the analytical methodology must have a



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corresponding low limit of detection. A number of speciation methods (separation and analysis) have been reported in connection with environmental monitoring studies; these have been reviewed by Brinckman (1983). More recently, Brinckman and coworkers have prepared a manuscript which presents a simple and rapid method for the speciation of aquatic samples using simultaneous hydridization/extraction with separation by gas chromatography and detection by flame photometry (Matthias et al. 1985). In using 100 mL salt water samples, the level of detection was said to be 7 ppt of tetrabutyltin, 7 ppt of tributyltin, 3 ppt of dibutyltin, and 22 ppt of monobutyltin.

Among the methods cited in this Support Document in connection with environmental monitoring or bioassay studies are those that measure the four butyltin species ($Bu_nSn$) and inorganic tin. They are based upon preliminary extraction and purification using an organic solvent (benzene, tropolone, hexane, methyl isobutylketone) followed by formation of a volatile derivative with a Grignard reagent (butyl-, pentylor hexylmagnesium bromide) or with sodium borohydride (hydride). Species separation is then accomplished by either gas chromatography (GC) or programmed warming in a purge/trap (PT) system with detection of the volatilized organotin derivative by atomic absorption spectroscopy (AA), flame photometric detection (FPD) or mass spectroscopy (MS). Detection limits for tributyltin (cation) in marine water columns have been reported at 7 ppt (Matthias et al. 1985, using hydridization and GC/FPD); 20 ppt (Maguire et al. 1982, using butyl or pentyl derivatives and either GC/FPD or GC/AA); 5 ppt (Valkirs et al. 1985, using hydrization and PT/AA); and, 5 ppt (Huggett 1985, using hexyl derivatives and GC/FPD with confirmation by MS). To achieve these detection limits sample volumes have varied from 500 mL to 2000 mL.

Since higher levels of TBT have usually been observed in surface microlayer, fish tissues and other sorbing media including sediment, analytical methods for these specimens have been cited with higher detection limits. These include 60 to 150 ppt for surface microlayers (Maguire 1982, using 100 mL samples by GC/FPD); 5000 ppt for marine sediment (Maguire 1982, using 1 gram dry specimens by GC/FPD); and, 80 ppt for fish tissue (Waldock and Thain 1983, on tissue using flameless AA).

## II. ASSESSMENT OF RISK

The EPA has determined that registered products and applications for registration of pesticide products containing the following active ingredients in antifouling paints: bis (tributyltin) oxide, bis(tributyltin) adipate, bis(tributyltin) dodecenyl succinate, bis(tributyltin) sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, and tributyltin resinate meet or exceed the existing criteria (40 CFR 162.11) and new risk criteria (50 FR 49003) for acute and chronic hazard to nontarget aquatic organisms.

Tributyltin compounds are very effective biocides, toxic to marine and freshwater organisms at extremely low concentrations. The use of tributyltin compounds in antifoulant paints, has resulted in increased concentrations of TBT in harbors, marinas, and estuaries. Environmental hazard to nontarget organisms (i.e., nonfouling organisms such as mussels, clams, and oysters) is highly probable, where TBT concentrations have been measured at or near the recorded acute and chronic toxicity levels for various nontarget aquatic organisms including commercially valuable marine organisms.

EPA has determined that the use of pesticide products containing bis(tributyltin) oxide, bis(tributyltin) adipate, bis(tributyltin) dodecenyl succinate, bis(tributyltin) sulfide, tributyltin acetate, tributyltin acrylate, tributyltin fluoride, tributyltin methacrylate, and tributyltin resinate when used in antifoulant paints exceeds the risk criterion for acute and chronic toxicity as defined in 40 CFR 162.11(a)(3)(i)(B) and 40 CFR 162.11 (a)(3)(ii)(C) which provide that a Special Review shall be conducted if a pesticide:

> "results in a maximum calculated concencentration following direct application to a 6-inch layer of water more than 1/2 the acute $LC_{50}$ for aquatic organisms representative of the organisms likely to be exposed . . ." (40 CFR 162.11(a)(3)(ii)(B))

Or if use of the chemical:

> "can reasonably be anticipated to result in significant local regional or national population reductions in nontarget organisms, or fatality to members of endangered species." (40 CFR 162.11(a)(3)(ii)(C))

The Agency has issued new Special Review regulations which include revised risk criteria. Although these criteria are not in place at the present, we have concluded that these TBT

products also meet or exceed the new risk criterion (50 FR 49003) because concentrations of TBT in the marine and freshwater aquatic environments may result

> "in residues of the pesticide product or its ingredients, impurities, metabolites, or other degradation products in the environment of nontarget organisms at levels which equal or exceed concentrations acutely or chronically toxic to such organisms . . . at levels which produce adverse reproductive effects in such organisms as determined from tests conducted on representative species or from other appropriate data."

This chapter consists of three sections. The first discusses the toxicity of TBT to nontarget aquatic organisms; the second presents the concentrations of TBT which have been found in the marine and freshwater environments; and the third section summarizes the potential risk posed by the use of TBT active ingredients in antifouling paint formulations.

## A. Toxicity of TBT to Nontarget Aquatic Organisms

### 1. Introduction

In this toxicity section, information summarizing the adequacy of historical bioassay tests and the acute and chronic toxicity of TBT to fish, algae, crustaceans, and molluscs will be summarized.

### 2. Measurement of Toxicity

Only recently have data been available on the toxicity and environmental fate of tributyltin compounds, especially with an interest toward delineating the relationship which may exist between the number of alkyl groups (i.e., tributyl, dibutyl, and monobutyl) and the toxicities of these compounds. Many studies were conducted as static bioassays with nominal non-measured (estimated) concentrations. Nominal values do not take into account the tributyltin adsorption onto test containers resulting in an overestimate of the actual available toxicant in the solution. Since the concentration of TBT toxicant can be overestimated, the $LC_{50}$ reported may underestimate the TBT toxicity (e.g., while the actual $LC_{50}$ may be 60 ppt, the reported value may be 100 ppt since the TBT concentration was not measured). This adsorption problem is critical at very low levels (i.e., < 1.0 ppb) where a 70 percent decrease (almost an order of magnitude) has been found between nominal and measured concentrations of tributlytin (M & T Chemical Co., Aug. 1977).

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Static renewal bioassay testing procedures may provide accurate estimates of tributyltin concentration if the test solution renewal period is brief; this procedure eliminates lengthy resident times and loss of tributyltin by adsorption and/or subsequent degradation to intermediate forms. Flowthrough bioassay testing with simultaneous chemical analyses for chemical speciation of the toxicant in solution is, however, a more desirable testing approach.

The detection limits of TBT concentration measurement are of major concern. TBT has been detected in water column samples using the borohydride method (Matthias et al. 1985) as low as 7 ppt. This method is most effective with large water sample sizes. The Virginia Institute of Marine Science (VIMS) has been able to detect levels of tributyltin as low as 2.0 ppt (Perkins 1985). The determination of environmental concentrations in water column samples is critical to the development of a risk assessment. The inability to measure low ppt levels of TBT can result in an erroneous assessment of hazard at the sublethal chronic level.

The following discussion characterizes the concerns EPA has regarding tributyltin toxicity to nontarget aquatic organisms subsequent to their exposure to TBT concentrations now found in harbors, marinas, lakes, and estuaries. Table 2 summarizes the TBT toxicity data used to initiate the Special Review. It should be noted that different investigators used different chemical forms (salts) of TBT in conducting the aquatic toxicity studies. These included the chloride, the bis(tributyltin) oxide and the methacrylate. Although $LC_{50}$ values were reported using these different forms of TBT, their effect on the final measured or calculated result is relatively negligible. For example, the molecular weight ratio between the bis(tributyltin) oxide and tributyltin chloride is only two-fold, whereas, the acute toxicities vary across species of fish by approximately 24-fold.

### 3. Toxicity to Fish

Acute toxicity testing usually measures the lethal ($LC_{50}$) or effective ($EC_{50}$) concentrations where 50 percent of the test organisms are killed or significantly affected. Acute toxicity of bis(tributyltin) oxide (TBTO) to certain freshwater fish appears to range from 0.96 ppb to 24.0 ppb. Reported 96-hour $LC_{50}$ values (nominal concentrations) for rainbow trout (Salmo gairdneri), bluegill (Lepomis macrochirus), channel cat fish (Ictalurus punctatus), and mummichog (Fundulus heteroclitus) were 6.9, 7.6, 12.0, and 24 ppb, respectively (M & T Chemical Co. Sept. 1976; Oct. 1976; June 1978). These studies were static nonrenewal, using nominal concentrations, and may not be sensitive indicators of actual toxicity (i.e., actual $LC_{50}$ levels could be 70 percent lower due to adsorption to test container surfaces and volatilization).

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| FISH | | | | | | |
| Lepomis macrochirus (Bluegill) | TBTO | 96-hr $LC_{50}$ = 7.6 ppb (5.6 to 10 ppb) | Nominal concentrations | Static | 5.6, 7.5, 10.0 and 14.0 ppb | M & T Chemical Co. (Oct. 1976) |
| Salmo gairdneri (Rainbow trout) | TBTO | 96-hr $LC_{50}$ = 6.9 ppb (6.27 to 7.8 ppb) | Nominal concentrations | Static | 4.1, 5.3, 6.8, 8.8, and 11.0 ppb | M & T Chemical Co. (June 1978) |
| Ictalurus punctatus (Channel catfish) | TBTO | 96-hr $LC_{50}$ = 12.0 ppb (7.3 to 20.0 ppb) | Nominal concentrations | Static | 7.5, 14.0, 18.0, 24.0 and 28.0 ppb | M & T Chemical Co. (Sept. 1976) |
| Fundulus heteroclitus (Mummichog) | TBTO | 96-hr $LC_{50}$ = 24.0 ppb | Nominal concentrations | Static | 32.0, 42.0, and 56.0 ppb | M & T Chemical Co. (Sept. 1976) |
| Salmo gairdneri (Rainbow trout) | TBTO | 24 hr $EC_{50}$ = 31.0 ppb (loss of positive rheotaxis). Level from 5850 ppb to 11.7 ppb. TBTO resulted in damage to gill epithelium. At 11.7 ppb there was a flattening of bile duct columnar epithelial cells and separation from connective tissue after 5-day exposure. Destruction of corneal epithelium occurred after 7-day exposure to 11.7 ppb. | Not reported | Continuous flow stainless steel tanks | 5850 to 11.7 ppb acetone | Chliamovitch & Kuhn (1976) |



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Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| Cyprinodon variegatus (Sheepshead minnow) 33 to 49 mm | TBTO | 21-day $LC_{50}$ = 0.96 ppb Total mortality at 3.2 ppb at 14 days. | AAS measured concentrations | 21-day flow-through acute testing | 0.33, 0.63, 0.70, 1.5, 3.2 acetone-methanol | Ward et al. (1981) |
| Cyprinodon variegatus (Sheepshead minnow) 17 to 25 mm | $^{14}C$-TBTO | The maximum observed bioconcentration factors were X2120 and X4580 for the head and viscera, respectively. After 58 days the depuration of $^{14}C$-TBTO from all tissues was rapid. (52% after 7 days). | LSC measured concentrations | Exposed to TBTO for 58 days. | 0.96 to 2.07 ppb acetone | Ward et al. (1981) |
| Salmo gairdneri (Rainbow trout yolk sac fry) | TBTCL | 10 to 12 day $LC_{100}$ = 5.0 ppb. Decrease in growth rate at 0.2 and 1.0 ppb for 110 days. Toxicity not observed at 0.2 and 1.0 ppb; hemoglobin concentration and erythrocyte count were reduced in blood; hyperplasia and diminished glycogen content observed in liver. | Nominal concentrations | 110-day continuous-flow exposure | 0, 0.2, 1.0, and 5.0 ppb | Seinen et al. (1981) |

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| ALGAE | | | | | | |
| Ankistrodesmus falcatus (Freshwater algae) | TBTO | A maximum algal bioconcentration factor of $3 \times 10^4$ was estimated for TBT after 7 days. | GC and FPD | Static | 20 ppb methanol | Maguire et al. (1984) |
| Skeletonema costatum (Marine diatoms) | TBTO | 72 hr $EC_{50}$ = 0.33 ppb | ICAP | Static Nominal (only stock measured) | 0.5, 1.0, 5.0, 7.5, 10.0, 15.0, and 25.0 ppb | Walsh et al. (1985) |
| Thalassiosira pseudonana (Marine diatoms) | TBTO | 72 hr $EC_{50}$ = 1.03 ppb | ICAP | Static Nominal (only stock measured) | 0.5, 1.0, 5.0, 7.5, 10.0, 15.0, and 25.0 ppb | Walsh et al. (1985) |

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| CRUSTACEANS | | | | | | |
| Crangon crangon (Shrimp) | TBTO | Larvae 96 hr $LC_{50}$ = 1.5 ppb. Adult 96 hour $LC_{50}$ = 41 ppb. | Not reported | Static renewal every 24 hours | Not reported | Thain (1983) |
| Acartia tonsa (Copepod) | TBTO | 72 hr $EC_{50}$ = 2.1 ppb<br>96 hr $EC_{50}$ = 1.0 ppb<br>144 hr $EC_{50}$ = 0.4 ppb | Measured concentrations AAS | Static renewal every 24 hours Pyrex test tubes | 0.3, 0.5, 1.0, 1.7, and 3.0 ppb acetone | U'ren (1983) |
| Homarus americanus (Lobster larvae) | TBTO | 90% decrease in growth at 1.0 ppb. | Nominal concentrations | Static renewal every 48 hours | 1.0, 5.0, 10.0, 15.0, and 20.0 ppb | Laughlin & French (1980) |
| Rhithroponopeus harrisii (Mud crab) | TBTO | Bioaccumulation of 4400X in the hepatopancreas. No steady state achieved. Accumulation of TBTO from food greater than from only the water | Measured concentration of $C^{14}$ radioassay. | Static renewal every 24 hours. Artemia with concentrations 1.23 ug TBTO/g wet weight were fed to crabs. | 0.28 ppb and 6.1 ppb | Evans & Laughlin (1984) |
| Daphnia magna (Water flea) | TBTO | 48 hr $LC_{50}$ = 1.67 ppb (1.01 to 2.5 ppb) | Nominal concentration | Static | 1.7, 3.0, 5.3, 7.1, and 13.3 ppb ethanol | M & T Chemical Co. (Jan. 1976) |

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| MOLLUSCS | | | | | | |
| Crassostrea virginica (Eastern oyster larvae) | TBTO | 48 hr $EC_{50}$ = 0.9 ppb (0.4 to 1.9 ppb) | Nominal Concentration | Static | 0.1, 0.3, 0.6, 1.0, 3.2, and 5.6 ppb | M & T Chemical Co (June 1977) |
| Crassostrea gigas (Pacific oyster larvae) | TBTO | 48 hr $LC_{50}$ = 1.6 ppb | Not reported | Static renewal every 24 hours | Not reported | Thain (1983) |
| Mytilus edulis (Mussel larvae) | TBTO | 48 hr $LC_{50}$ = 2.3 ppb | Not reported | Static renewal every 24 hours | Not reported | Thain (1983) |
| Mytilus edulis (Mussel larvae) | TBTO | 15 day $LC_{50}$ = 0.1 ppb long-term effect | Measured concentrations FAAS | Static renewal every 72 hours | 10.0, 1.0, and 0.1 ppb | Beaumont & Budd (1984) |
| Crassostrea gigas (Pacific oyster spat) | Exposure for 45 days to tributyltin methacrylate leachates | Significant reduction in growth at 0.24 ppb | Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method) | Flow-through | 0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level | Thain & Waldock (1985) |
| Mytilus edulis (Mussel spat) | Exposure for 45 days to tributyltin methacrylate leachates | Significant reduction in growth at 0.24 ppb | Measured daily for 3 weeks and every other day for the remainder | Flow-through | 0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level | Thain & Waldock (1985) |

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Reference |
|---|---|---|---|---|---|---|
| Mytilus edulis (Mussel spat) (Continued) | | | of the experiment (M&T standard method) | | | |
| Venerupis decussata (Clam spat) | Exposure for 45 days to tributyltin methacrylate leachates | Significant reduction in growth at 0.24 ppb | Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method). | Flow-through | 0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level | Thain & Waldock (1985) |
| Ostrea edulis (European oyster spat) | Exposure for 45 days to tributyltin methacrylate leachates | Growth inhibited at 2.6 ppb | Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method). | Flow-through | 0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level | Thain & Waldock (1985) |
| Venerupis semidecussata (Clam spat) | Exposure for 45 days to tributyltin methacrylate leachates | Growth inhibited at 2.6 ppb | Measured daily for 3 weeks and every other day for the remainder of the experiment (M&T standard method). | Flow-through | 0.24 ± 0.23 ppb for low-level and 2.62 ± 1.09 ppb for high level | Thain & Waldock (1985) |

Table 2. Test Conditions, Procedures, and Results of Tributyltin Toxicity Tests (Continued)

| Test Organism | Organotin Compound | Effect | Analytical Methods | Type of Exposure | Concentration Levels | Referenc |
|---|---|---|---|---|---|---|
| Ostrea edulis (European oyster spat) | TBTO | Growth effected at 0.02 ppb (marginal). At 0.06 ppb growth rate was severely curtailed after 10 days. | Nominal concentration renewed every day. (M&T standard method). | Static renewal 24 hours | 0.02 to 2.0 ppb | Thain & Waldock (1985) |
| Crassostrea gigas (Pacific oyster) | TBTO | Bioaccumulation of 2000 to 6000 fold after 22 days (poor diet was noted). | FAAS measured for the first 5 days of exposure and | Flow-through | 0.15 and 1.25 ppb | Waldock, Thain, an Miller (1983) |
| Ostrea edulis (European oyster) | TBTO | Bioaccumulation of 1000 to 1500 fold after 22 days (poor diet was noted). | FAAS measured for the first 5 days of exposure and on alternate days until the completion. | Flow-through | 0.15 and 1.25 ppb | Waldock, Thain, an Miller (1983) |
| Crassostrea gigas (Pacific oyster spat) | TBTO | Spat grew poorly at TBT concentrations of 0.15 ppb; developed pronounced thickening of upper shell valve. Bioconcentration (Flesh) after 56 days exposure to 0.15 ppb was about X11400 fold. | FAAS measured (M&T Standard method) | Static renewal 24 hours | 0.08 to 1.2 ppb | Waldock & Thain (1983) |
| Nassarius obsoletus (Mud snail) | Alumacide TBT paint | Anatomical abnormality consisting of superimposition of male characteristics on female snails. | Not reported | Not reported | Not reported | Smith (1981) |

GC = Gas Chromatography
FPD = Flame Photometric Detection
ICAP = Inductively Coupled Argon Plasma
FAAS = Flameless Atomic Absorption Spectrophotometry
LSC = Liquid Scintillation Counting

Ward (Ward et al. 1981) found that sheepshead minnow (Cyprinodon variegatus) exposed to TBTO for 21 days (measured flowthrough system) had an $LC_{50}$ of 0.96 ppb and total mortality in 14 days at a concentration of 3.2 ppb. It was further noted that after exposure to TBTO (0.96 to 2.07 ppb) for 58 days, the maximum observed bioconcentration factors were 2120X and 4580X for head and viscera, respectively. He also noted that after an additional 58 days (i.e., 116 days total) the depuration, or elimination, of TBTO from all tissue was rapid (52% after 7 days post-exposure).

Chronic effects on fish were found by Seinen et al. (1981) after subjecting rainbow trout yolk sac fry to 110 day exposure to concentrations of tributyltin chloride (continuous-flow exposure, nominal concentrations). A 10 to 12 day $LC_{100}$ of 5 ppb was estimated using concentration levels 0.2, 1, and 5 ppb. Although, young trout exposed to tributyltin chloride concentrations of 0.2 and 0.1 ppb did not exhibit mortality, there was a significant reduction in growth (40% decrease in body weight), decrease in hemoglobin content, hyperplasia of liver cells, and diminished glycogen content in liver. Chilamovitch and Kuhn (1976) noted histological and hematological effects on rainbow trout after continuous exposure to TBTO. Damage to gill epithelium was recorded at 1.7 ppb. At 11.7 ppb with 5 days of exposure, there was a flattening of bile duct columnar epithelial cells and separation of these cells from connective tissue. Destruction of corneal epithelium was observed following 7 days of exposure to 11.7 ppb.

4. Toxicity to Algae

The toxicity of tributyltin compounds to algae has not been intensively studied. Maguire et al. (1984) noted that the freshwater algae (Ankistrodesmus falcatus) possesses a mechanism for sequential debutylation of TBTO. However, Walsh et al. (1985) found that TBTO inhibited population growth and cell survival of marine unicellular algae Skeletonema costatum and Thalassiosira pseudonana at low concentrations (72 hour $EC_{50}$ of 0.33 ppb and $EC_{50}$ of 1.03 ppb, respectively).

5. Toxicity to Crustaceans

The toxicity of tributyltin to crustaceans was evaluated by several researchers. Laughlin (1980) using nominal concentrations in a static daily renewal, found that lobster larvae (Homarus americanus) exhibited a 90 percent decrease in growth at 1 ppb. U'ren (1983) calculated a 144 hour $EC_{50}$ for marine copepods (Acartia tonsa) at 0.4 ppb (measured concentrations static daily renewal). Thain (1983) reported 96 hours $LC_{50}$ values for larvae and adult shrimp (Crangon crangon) at 1.5 and 41 ppb, respectively.

Tributyltin bioaccumulation in crustaceans was demonstrated by Evans and Laughlin (1984) with their work on mud crabs (Rhithroponopeus harrisii) exposed to radiocarbon labeled TBTO. The test measured the short-term effects of exposure to labeled test concentrations in water (0.28 ppb) and food (Artemia, 1.23 ppb). Four-day bioaccumulation factors ranged up to 4400 in the hepatopancreas with no indication that a steady state equilibrium had been approached. Accumulation of tributyltin from food was greater than that from the water.

6. Toxicity to Molluscs

Acute toxicity of TBTO to certain molluscs appears to range from 0.1 to 2.3 ppb. Reported 48-hour $LC_{50}$ values for Eastern oyster larvae (C. virginica), Pacific oyster larvae (C. gigas) and mussel larvae (M. edulis) were 0.9, 1.6 and 2.3 ppb, respectively (M & T Chemical Co. June 1977; and Thain 1983). A 15-day $LC_{50}$ of 0.1 ppb was also reported for mussel larvae (M. edulis) (Beaumont and Budd 1984).

Anatomical abnormalities attributed to tributytins were found in certain intertidal mud snails (Massarius obsoletus) living near yacht basins (Long Island Sound and Southport, CT). Smith (1981), by investigating this phenomenon it was noted that these dioecious snails had developed male characteristics on apparently normal female reproductive anatomy. The correlation between tributyltin concentration and these abnormalities was later confirmed in laboratory studies.

European researchers have found a significant correlation between the TBTO concentration levels in certain estuarine areas and shellfish deformity. Waldock and Thain (1983) in England found that Pacific oyster (Crassostrea gigas) spat (set oyster larvae) grew poorly in TBTO concentrations of 0.15 ppb, and developed pronounced thickening of the upper shell valve. Bioconcentration factors, after 56 days exposure to 0.15 ppb TBTO, were 11,400X. Alzieu et al. (1980) observed similar malformations in C. gigas and attributed it to the presence of organotin (TBTO and TBTF) in the French shellfish regions. Beaumont and Budd (1984) noted that common mussel (Mytilus edulis) larvae did not survive past 5 days at a TBTO exposure concentration of 10 ppb, or longer than 10 days at a TBTO level of 1 ppb. They concluded that the high TBT levels found at several estuarine sites are associated with adult shellfish population reductions in these areas (a 15 day $LC_{50}$ of 0.1 ppb was estimated). Thain and Waldock (1985) tested several shellfish larvae with tributyltin methacrylate leachates in measured flow-through systems. They found that Pacific oyster (Crassostrea gigas), mussel (Mytilus edulis), and clam (Venerupis decussata) showed a significant reduction in growth at 0.24 ppb. A static renewal (nominal concentrations) test with spat of the European flat oyster (Ostrea edulis) demonstrated that growth rate was severely curtailed following exposure to 0.06 ppb TBTO.

According to Waldock and Thain (1983), oysters (C. gigas and O. edulis) rapidly bioaccumulate TBT and reach an equilibrium uptake after exposure, and subsequently are slow to depurate this uptake. Using measured concentrations in a 21-day continuous-flow system, Waldock and Thain exposed C. gigas and O. edulis (10 g wet weight) to TBTO concentrations of 1.25 and 0.15 ppb. C. gigas accumulated a high body level of tributyltin that ranged from 2000- to 6000-fold. O. edulis maintained under the same conditions only concentrated tributyltin from 1000- to 1500-fold. This twofold to fourfold difference in tissue concentration of tributyltin between species correlates with the threefold to ninefold difference found in the field.

The probability of food chain accumulation was addressed by Laughlin, French, and Guard (1984), studying tributyltin uptake by marine mussels (Mytilus sp.). TBT bioaccumulated from 1000 to 6000 times and was attributed more to food intake than to direct absorption from water or sediment.

Given its high lipophilicity TBT is likely to be bioaccumulated by several organisms. Laboratory studies may underestimate the extent of bioaccumulation as they are generally of insufficient duration to allow all compartments within the test vessel (food material, feces, water, test organisms, vessel walls, etc.) to reach equilibrium. Studies are needed to evaluate the subsequent toxicity problems associated with high bioaccumulation of TBT.

B. Exposure: TBT in the Marine and Freshwater Environment

In addition to review of available bioassay and aquatic toxicity data, the Agency has also evaluated data available on TBT concentrations in water samples analyzed from both marine and freshwater environments. Analytical methods sensitive to the ppt level have only recently been developed and monitoring data using this new methodology are currently very limited. Some of this information is shown in Table 3. Data from Canadian harbors in Lake Superior and Lake Ontario are included to provide some indication of the likely contamination levels in Great Lakes harbors and other freshwater bodies with similar water craft use patterns.

The data from San Diego Bay, at present, is one of the most systematic analyses of tributyltin levels in a U.S. bay or estuary (Valkirs et al., 1985). On the basis of informal surveys of local retail outlets, Valkirs and coworkers estimated that the use of tributyltin on recreational craft in this bay greatly increased during the course of the study. This appears to be reflected by a sharp elevation in the concentration of TBT in the waters near Shelter Island Yacht harbor where a study maximum of 930 ppt tributyltin was measured. This investigation in the Shelter Island waters is particularly significant because

antifouling paints are likely to have been the only source of tributyltin in that area (i.e. there are no drydock TBT discharges or other TBT point discharges identified in the area). In relation to the entire San Diego Bay study, it should be noted that, although tributyltin is thought to readily bind to sediment, (U.S. Naval Sea Systems Command 1984) divers taking discrete water samples 10 cm above the bottom sediments found approximately the same concentrations as were detected in surface water samples. Figure 1 identifies the location of the sampling stations.

The monitoring data discussed above may not be totally comparable to values ($LC_{50}$'s etc.) reported in aquatic toxicity studies. Most aquatic toxicity studies are conducted with filtered water into which the toxin has been initially dissolved. The monitoring data reviewed above represent unfiltered water analyses which would, perhaps, include sediment bound toxin and even, perhaps, tributyltin which had been assimilated into planktonic organisms. Further investigation as to whether or not a large proportion of aqueous TBT would be in a bound form is needed. If binding is found to be significant then the toxicological significance will have to be determined.

There is also reason to believe that the monitoring data might underestimate the hazard. The Great Lakes and Chesapeake Bay researchers with whom the Agency has been in direct contact state that none of their samples have been taken in the late spring when freshly painted boats would be launched. Monitoring by Waldock and Miller (1983) in an English estuary found highest annual concentrations in May (corresponding to the postwinter launching of pleasure craft).

In addition to the samples noted in Table 3 are samples collected by Virginia Institute of Marine Science (VIMS) upstream and downstream (as influenced by tidal action) from large commercial ships moored near the Elizabeth River in Hampton Roads. The concentration of tributyltin above the ships was approximately 5 ppt. The concentration in the surface water downstream from ships was 13 ppt. Figure 2 identifies the sampling stations used for the VIMS one day study.

Attempts were made during the Annapolis and Great Lake studies to measure the concentration of tributyltin in the surface microlayer--where high concentrations of lipophilic pesticides have been found, as noted from other studies in the literature. Contamination of the water surface is presumed to be injurious to floating fish eggs such as croaker, herring, and shad species. Unfortunately no completely satisfactory method of sampling such a thin layer of the water column is available.

Table 3. Tributyltin Concentrations (ng/L = ppt) for Water Samples)[1] Collected at Indicated Stations with Analytical Method Noted

| Location | Concentration (ppt $TBT^+$) | Sample Type Depth (Meters) | Analytical Method | Ref. |
|---|---|---|---|---|
| Annapolis, MD Across harbor from city docks | 34 | 1 | Hydride derivitization, GC/FPD | 1 |
| Marina in Back Creek | 71 | 1 | Hydride derivitization, GC/FPD | 1 |
| Lake Superior (Marathon) | 20 | 5 | Pentyl derivitization GC/FPD | 2 |
| Lake Ontario (Toronto Harbor) | 840 | 5 | Pentyl derivitization GC/FPD | 2 |
| Lake Ontario (Hamilton Harbor) | 160 | 5 | Pentyl derivitization GC/FPD | 2 |
| Lake Ontario (Whitby Harbor) | 50 | 5 | " | 2 |
| San Diego Bay[2] Station 3-2 | | | | |
| 3 Jan 83 | 50 | 0.3-0.6 | Hydride derivitization, AA[4] | 3 |
| | 130 | Bottom[3] | " | 3 |
| Station 3-3 | | | | |
| 3 Jan 83 | 100 | 0.3-0.6 | " | 3 |
| " | 550 | Bottom | | |
| 14 Feb 84 | 180 | 0.3-0.6 | " | 3 |
| Station 3-4 | | | | |
| 3 Jan 83 | 10 | 0.3-0.6 | " | 3 |
| " | 110 | Bottom | " | 3 |
| Station 4 | | | | |
| 3 Jan 83 | ND | 0.3-0.6 | " | 3 |
| " | 30 | Bottom | " | 3 |
| 14 Feb 84 | 30 | 0.3-0.6 | " | 3 |
| Station 5 | | | | |
| 3 Jan 83 | ND | 0.3-0.6 | " | 3 |
| " | ND | Bottom | " | 3 |
| 14 Feb 84 | 10 | 0.3-0.6 | " | 3 |
| San Diego Bay Station 1 | | | | |
| 3 Jan 83 | ND | 0.3-0.6 | Hydride dervitization, AA | 3 |
| " | 10 | Bottom | " | 3 |

Table 3. Tributyltin Concentrations (ng/L = ppt) for Water Samples[1/] Collected at Indicated Stations with Analytical Method Noted (Continued)

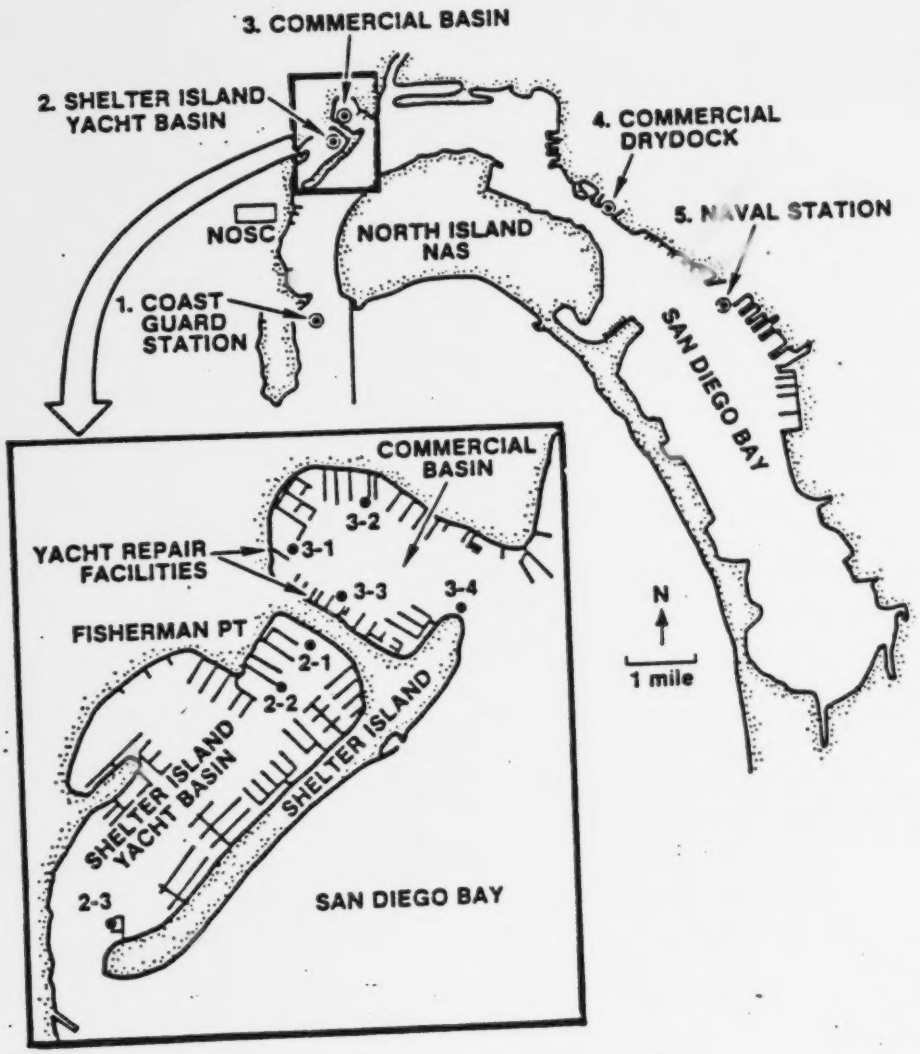
| Location | Concentration (ppt $TBT^{+}$) | Sample Type Depth (Meters) | Analytical Method | Ref. |
|---|---|---|---|---|
| San Diego (Cont.) | | | | |
| Station 2-1 | | | | |
| 3 Jan 83 | 60 | 0.3-0.6 | Hydride derivitization, AA | 3 |
| " | 100 | Bottom | " | 3 |
| 20 Jun 84 | 270 | 0.3-0.6 | " | 3 |
| 7 Mar 85 | 290 | 0.3-0.6 | " | 3 |
| 25 Sep 85 | 780 | 0.3-0.6 | " | 3 |
| Station 2-2 | | | | |
| 3 Jan 83 | 50 | 0.3-0.6 | " | 3 |
| " | 60 | Bottom | " | 3 |
| 14 Feb 84 | 350 | 0.3-0.6 | " | 3 |
| 2 Jul 85 | 490 | 0.3-0.6 | " | 3 |
| 25 Sep 85 | 930 | 0.3-0.6 | " | 3 |
| Station 2-3 | | | | |
| 3 Jan 83 | 20 | 0.3-0.6 | " | 3 |
| " | 40 | Bottom | " | 3 |
| 14 Feb 84 | 200 | 0.3-0.6 | " | 3 |
| Station 3-1 | | | | |
| 3 Jan 83 | 180 | 0.3-0.6 | " | 3 |
| " | 140 | Bottom | " | 3 |
| 14 Feb 84 | 200 | 0.3-0.6 | " | 3 |
| 18 Dec 84 | 210 | 0.3-0.6 | " | 3 |
| Elizabeth River, Near Norfolk, Va[5/] | | | | |
| 16 Sep 1985 | | | | |
| Station 1 | 6 | 1 | Hexyl derivitization | 4 |
| Station 2 | 6 | 1 | " | 4 |
| Station 3 | 7 | " | " | 4 |
| Station 4 | 12 | " | " | 4 |
| Station 5 | 21 | " | " | 4 |
| Station 6 | 63 | " | " | 4 |
| Station 7 | 49 | " | " | 4 |
| Station 8 | 39 | " | " | 4 |

1/ All water samples were whole. No filtered samples were made.
2/ See Figure 1 for location of sampling stations.
3/ Bottom samples were taken 10 cm from the bottom by scuba divers.
4/ AA Hydrogen flame atomic absorption spectrophometry.
5/ See Figure 2 for location of sampling stations.

References

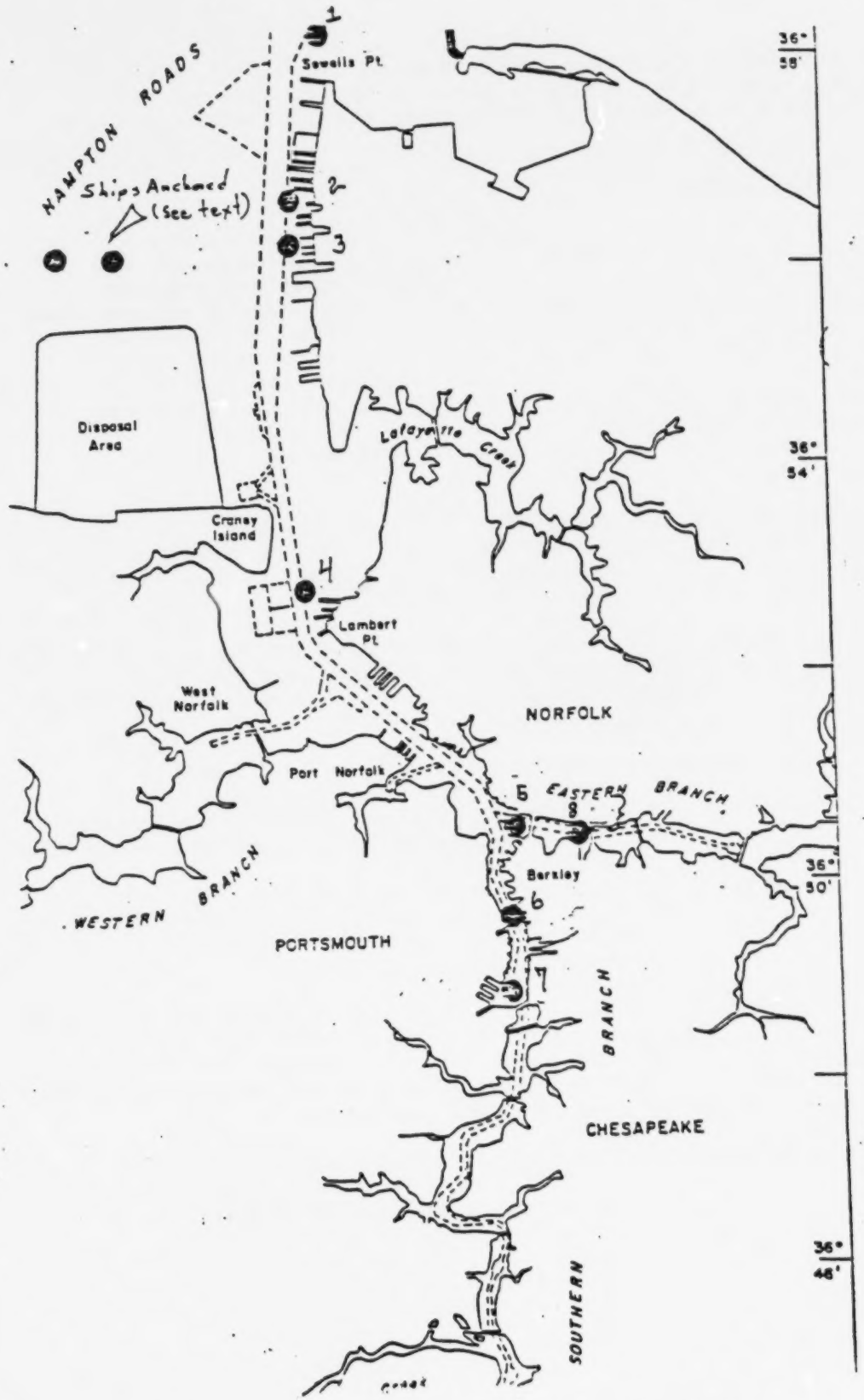
1. Matthias et al. 1985.
2. Macguire et al. 1982.
3. Valkirs et al. 1985.
4. Perkins 1985.

Figure 1. Navy Sampling Stations in San Diego Bay[1]/




[1]/ Valkirs et al. 1985.

Figure 2. Virginia Institute of Marine Science Sampling Stations in the Elizabeth River Estuary[1/]




1/ R.J. Huggett, Virginia Institute of Marine Science



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Both the Annapolis and Great Lakes studies indicated, however, that the concentration is much higher in the microlayer and the Agency is concerned about risks that this contamination may pose.

C. Risk Summary

After extensive evaluation of published reviews, consultation with various Federal and State laboratories, and review of EPA data files, EPA has concluded that tributyltin (TBT) in antifouling paints may be a potential hazard to nontarget aquatic organisms in areas of high boat traffic, marinas, and estuaries. The toxicity and threat of TBT exposure to aquatic organisms satisfies the existing risk criteria (40 CFR 162.11) and the new risk criteria (50 FR 49003) for acute and chronic hazards to nontarget aquatic organisms as defined earlier in this chapter. A summary of aquatic toxicity values is presented as follows:

1) Molluscs: Acute $LC_{50}$ = 0.1 to 2.3 ppb
Chronic effects: 0.06 to 0.24 ppb
Bioaccumulation: 2000- to 11,000-fold; very slow depuration.

2) Fish: Acute $LC_{50}$ = 0.96 to 24.0 ppb
Chronic effects: 0.2 to 10.0 ppb
Bioaccumulation: 2120- to 4580-fold; rapid depuration.

3) Crustaceans: Acute $LC_{50}$ = 0.3 to 41.0 ppb
Chronic effects: 1.0 ppb
Bioaccumulation: 4400-fold; greater accumulation from food than from water.

4) Algae: Acute $LC_{50}$ = 0.33 to 1.03 ppb
Bioaccumulation: 8000- to 30,000-fold; toxic in some species, depuration in others.

Environmental concentrations of tributyltin are listed in Table 3. Several locations appear to have tributyltin concentrations equal to, or greater than, toxicity values for nontarget aquatic organisms. The following conclusions may be made regarding toxicity and exposure at some of the locations:

1) Annapolis: tributyltin concentrations of .034 to .071 ppb may cause acute mollusc, and chronic mollusc effects.

2) San Diego Bay: tributyltin concentrations of .01 to .93 ppb may cause acute and chronic effects in several aquatic taxa (i.e., fish, mollusc, crustaceans, algae).

3) Lake Superior: tributyltin concentrations of .02 ppb may cause chronic mollusc effects.

4) Lake Ontario: tributyltin concentrations of .05 to .84 ppb may cause acute and chronic effects in several aquatic taxa (i.e., fish, mollusc, crustaceans, algae).

5) Norfolk, VA: tributyltin concentrations of .006 to .06 ppb may cause chronic mollusc effects.

EPA is concerned about the acute and chronic toxicity potential of tributyltin compounds to nontarget aquatic organisms. Water samples have been found to contain TBT levels that may have direct affects on aquatic organism populations (molluscs). The TBT compounds may bioaccumulate in aquatic biota and may pose a hazard to the food chain as they are passed from lower to higher trophic levels. Adsorption of tributyltin compounds to sediment may have long-term toxicity effects on benthic browsing organisms (crustaceans, snails, etc.). Contamination of estuarine areas at sublethal concentrations can influence fecundity of several aquatic taxa from fish to zooplankton, thus influencing population dynamics. The present use of tributyltin in antifouling paints presents a potential hazard to nontarget aquatic organisms.

The tributyltin compounds are acutely and chronically toxic to molluscs at low levels (0.06 to 2.3 ppb) depending upon molluscs species. A correlation between environmental concentrations of tributyltin and declining populations of nontarget organisms has been demonstrated in Europe through the works of Waldock and Thain, Beaumont, and Alzieu. Laboratory toxicity testing, environmental monitoring, and bioaccumulation studies have corroborated the conclusion that tributyltin antifouling paints may be responsible for the decline of several mollusc populations.

Based on these findings, Great Britain and France have regulated or curtailed the use of tributyltins in antifouling paints. Effective January 1, 1986 Great Britain is banning: a) copolymer formulations containing more that 7.5% organotin (measured as tin in the dry paint film) and b) those paints

based on copper or other antifouling systems containing more than 2.5% organotin (measured in the same way). In effect (b) will ban the supply of existing "free association" paints while allowing the minimum use of tributyltin compounds as a performance booster in other antifouling systems Great Britain will review these levels in time for the 1987 painting season with a view to reducing them in line with advances in paint technology. In addition, the British government proposes to establish an ambient water quality target for organotin concentrations.

France has recently extended its ban another 2 years on use of organotin paints for all boats less than 25 meters in length. The French experience shows that a ban on the use of TBT on pleasure craft can be highly effective. In 1982 the industry producing organotin compounds measured concentrations in Arcachon Bay and found levels 3 times higher than those known to cause malformation in Pacific Oysters. Since the implementation of the first ban (1983 to 1985), the recovery of oysters has been carefully monitored. In the Arcachon Bay in 1980 and 1981, C.gigas were very badly affected. Within some areas, 95-100% of the two year old oysters showed deformation of the shells. In 1982, the first effective year of the ban, the incidence of shell deformation was down to 70-80% and in 1983 to 45-50%. Even more important has been the reduction in number of oysters from the same areas showing deformities in both upper and lower shells. This was between 70 and 90% in 1980 and 1981 but zero in 1983. A similar recovery has occurred with spatfall; in 1980 and 1981 there was none, but in 1982 it was good and in 1983 it was excellent (Vosser 1985).

## III. BENEFITS

The Agency will perform a benefits analysis for the tributyltins during the Special Review. The following information summarizes available information on the usage of tributyltin antifoulant paints.

### A. Antifoulant Paint Use Pattern

Antifouling paints containing TBT or copper compounds are applied primarily to vessel hulls to control the growth of fouling organisms. The paints are also used to control fouling organisms on docks, buoys and other marine structures. Fouling is caused by the attachment of marine organisms to surfaces that are submerged or in contact with fresh or salt water. Species which cause fouling include algae, bacteria, barnacles, tubeworms, hydroids, and sponges. These organisms increase hull friction and weight which reduces speed and increases fuel consumption. In addition, fouling may cause deterioration to the hull coatings, possibly resulting in corrosion.

Antifouling paints containing tributyltin(s) are registered for use on wood, fiberglass, aluminum, steel, and cement hulls. These paints are applied to pleasure crafts, commercial vessels, and military ships. The U.S. Navy, the major domestic user of antifouling paints, is considering a conversion from cuprous oxide to a combination of tributyltin compounds and cuprous oxide in its antifouling paints. The Navy has proposed to use a copolymer paint with very low leach levels to minimize the the environmental loading of tributyltins.

The U.S. Navy is planning to replace the copper-based paints it is currently using on its steelhulled vessels with copolymer antifouling paints containing tributyltin and copper compounds. Five to twenty percent of the fleet would be treated annually with full replacement anticipated by 1991 at the earliest. A maximum annual increase of 100 vessels would be treated with an average of 900 pounds of tributyltin per vessel, constituting an additional use of approximately 90,000 pounds of tributyltin active ingredient per year (U.S. Naval Sea Systems Command 1984).

### B. Tributyltin Antifoulant Paint Registrations

As earlier indicated, nine tributyltin compounds are registered for use in antifouling paints. The TBT antifoulant paints are formulated as single active ingredient formulations, as multiple TBT formulations, as any one of the TBT's in combination with copper-based compounds (usually cuprous oxide), and as multiple TBT's plus copper-based compound formulations.

There are approximately 340 federally registered antifouling paints containing tributyltin active ingredients. Review of these registrations indicates that the most frequently registered tributyltins are bis(tributyltin) oxide (161 registrations), tributyltin fluoride (141 registrations), and tributyltin methacrylate (52 registrations). The 152 single active ingredient formulations generally range between 5 and 20 percent active ingredient. In formulations with two or more tributyltin compounds, active ingredients generally range from 6 to 13 percent. In formulations with tributyltins and copper compounds, tributyltins range from less than 1 to 20 percent. The number of free association paint formulations as compared to the copolymer paint formulations is not known at this time.

C. Usage of Tributlytin Antifoulant Paints and Alternatives

Current annual domestic usage of TBT pesticides for all uses including industrial processing water, nonindustrial processing water, wood preservatives, and antifouling paints, is estimated at approximately 730,000 to 860,000 pounds of active ingredients. Current domestic usage of tributyltins in antifouling paints ranges between 250,000 to 300,000 pounds active ingredient annually. Bis(tributyltin) oxide, accounts for 75,000 to 100,000 pounds used annually, or approximately one-third the tributyltin used as an antifoulant. Estimated annual antifoulant usage is 100,000 to 125,000 pounds of tributyltin methacrylate, 60,000 to 70,000 of tributyltin fluoride, 7,500 to 15,000 pounds of bis(tributyltin) adipate, and 5,000 to 10,000 pounds of tributyltin acetate. Tributyltin acrylate and tributyltin resinate annual usage are quite low, on the order of a few hundred pounds each. There appears to be no recent usage of bis(tributyltin) dodecyl succinate, and bis(tributyltin) sulfide.

Many TBT antifoulant paints contain copper, or copper containing compounds, and cuprous oxide is still the main alternative to tributyltin in paint formulations. Other copper compounds, such as metallic copper, are also registered for use. Copper compounds are effective against the same antifouling organisms as the tributyltins; however, they tend to be corrosive to metal, especially aluminum. An insulative coating is recommended on steel hulls prior to copper-based antifoulant paint application. Label recommendations generally do not recommend copper-containing paints for aluminum boat hulls.

Depending upon the type of paint and whether there is copper or tributyltin biocides in the formulation, the antifouling compound may be leached from the paint, activated by periodical scrubbing of the outer paint layer, or exposed by gradual erosion of the paint as the vessel moves through the water (ablative process). The ablative process is the newest antifouling system in which the pesticide is part of the paint polymer. As the

vessel moves through the water, the outer paint layer is removed and a new layer of the antifouling paint is activated. The advantage of ablative paints is that they eliminate the requirement for scrubbing the underwater hull surface. Tributyltin paints are not corrosive to metal such as aluminum and eliminate the need for a protective coating between the metal and the antifouling paint, except when copper compounds are included in the paint formulation. Tributyltins also provide longer protection against antifouling organisms than the more commonly used cuprous oxide compounds, thus reducing a ship's drydock time.

D. Benefits of TBT Usage

Sufficient data are currently unavailable to the Agency to determine the use patterns and possible cost savings attributable to current and planned applications of TBT antifouling paints on commercial, recreational, and nonnaval military vessels.

The U.S. Navy Environmental Assessment stated that the conversion from nonablative copper-based paints to ablative tributyltin paints will result in fuel savings, elimination of underwater hull cleaning, and increased operational readiness. The U.S. Navy estimated that use of tributylin paints would result in a 15 percent savings in fuel consumption, amounting to an annual savings of $150 million once the entire fleet is treated with these paints. Eliminating the need for underwater hull cleaning between maintenance overhauls would save an estimated $5 million annually. Increased operational readiness, which is not amenable to quantification, relates to less time in port, longer range, and greater speed (U.S. Naval Sea Systems Command 1984).

## IV. OTHER REGULATORY CONSIDERATIONS

### A. Expansion of Special Review

The Special Review of bis(tributyltin) oxide, bis (tributyltin) adipate, bis(tributyltin) dodecenyl succinate, bis(tributyltin) sulfide, tributyltin acetate, tributyltin acrylate, tributyltin flouride, tributyltin methacrylate, and tributyltin resinate is being initiated based on acute and chronic toxicity to nontarget aquatic organisms. The focus of the review, at this time, is on the use of these compounds as antifoulant paints. However, if information evaluated during the Special Review indicates that the use of these compounds on other sites (including but not limited to cooling towers, textiles, etc.), results in exposure to nontarget aquatic organisms, or that any other criteria are met or exceeded, the Special Review may be expanded to include those pesticidal uses as well. Additionally, because most tributyltins pose similar toxicity to nontarget aquatic organisms, and several tributyltin compounds, in addition to the nine compounds under Special Review, are registered for sites which may result in exposure to nontarget aquatic organisms, the Special Review may be expanded to include a much larger subset of the tributyltin compounds than the original nine. These additional chemicals include:

Tributyltin Compounds

| Code No. | Chemical |
|---|---|
| 083102 | Bis(tributyltin) salicylate |
| 083103 | Bis(tributyltin) succinate |
| 083104 | Bis(tributyltin) sulfosalicylate |
| 083106 | Tributyltin benzoate |
| 083107 | Tributyltin chloride |
| 083108 | Tributyltin chloride complex of ethylene oxide condensate of abietylamine |
| 083109 | Tributyltin linoleate |
| 083110 | Tributyltin monopropylene glycol malate |
| 083111 | Tributyltin neodecanoate |
| 083115 | Tributyltin isopropyl succinate |
| 083118 | Tributyltin maleate |

At this time the Special Review is based on chronic and acute toxicity to nontarget aquatic organisms; however, the Agency is also concerned about the toxicity of these compounds to humans.

The animal toxicity data base to assess potential human toxicity is highly deficient for all TBT compounds under review (Doherty Memo Dec. 11, 1985) although there are some useful studies particularly with tributyltin oxide. The available information (obtained mostly with tributyltin oxide) indicates concerns over immunotoxicity, teratogenicity, dermal toxicity, inhalation toxicity, and endocine effects. The Agency cannot evaluate any human risks associated with the use of TBT compounds at this time both because the effects are not adequately studied and because we have no reliable estimates of exposure either through the food chain (e.g. oysters) or directly through use (e.g. applicators). Should new information enable the Agency to identify a potential human health trigger, the Special Review may be expanded to include such risks.

The Agency is also concerned that the use of TBT pesticidal products may adversely affect one or more endangered species. If information is obtained which supports this concern, the Special Review may be expanded to include consideration of these hazards.

B. Data Call-In Notices

The Agency also intends to issue Data Call-In Notices under the authority of section 3(c)(2)(B) of FIFRA. This section of FIFRA provides the Administrator with the authority to require that information be provided to the Agency, which is determined necessary to support the continued registration of a pesticide product. It also provides the authority to set specific timeframes for conducting the required studies and providing the data to the Agency. The Agency may issue a notice of intent to suspend registrations of affected products if registrants fail to comply with the requirements of the notices.

Data Call-In Notices are being developed requiring data for the nine tributyltin compounds under Special Review. Data required will include, at a minimum, leaching rate data by paint formulation, acute and chronic bioassay studies, bio-accumulation and biomagnification data, analytical methodology, environmental transport data, environmental monitoring data, and monitoring of exposure to workers applying and removing paints, as well as data quantifying TBT residues in fish and shellfish, and the volume of active ingredient used on the various sites for which these products are registered. Additionally, the Agency will conduct a comprehensive review of the data needed to support registrations of other tributyltin pesticidal active ingredients and may issue additional Data Call-In Notices concerning other tributyltin compounds.

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